16. Strutinskiy, V. B. Tribotekhnicheskie issledovaniya polimernyh kompozitov, primenyaemyh pri vosstanovlenii napravlyayushchih stankov [Text] / V. B. Strutinskiy, A. V. Radionenko, E. A. Ishchenko // Problemi tertya ta znoshuvannya. – 2015. – Issue 2 (67). – P. 4–11.
17. Sparham, M. Cutting force analysis to estimate the friction force in linear guideways of CNC machine [Text] / M. Sparham, A. A. D. Sarhan, N. A. Mardi, M. Dahari, M. Hamdi // Measurement. – 2016. – Vol. 85. – P. 65–79. doi: 10.1016/j.measurement.2016.02.017
18. Radionenko, A. V. Tribometr dlya issledovaniya vliyaniya kachestva poverhnostey na sostoyanie smazochnoy plenki [Text] / A. V. Radionenko // Mashinovedenie. – 1987. – Issue 6. – P. 93–97.
19. Kindrachuk, M. V. Osobennosti perekhodnyh rezhimov treniya poverhnostey s chastichno regulyarnym mikrorel'efom [Text] / M. V. Kindrachuk, A. V. Radionenko // Problemi tertya ta znoshuvannya. – 2016. – Issue 2 (71). – P. 4–13.

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STUDY INTO FORMATION OF COBALT-CONTAINING PEO-COATINGS ON AK12M2MGN FROM A PYROPHOSPHATE ELECTROLYTE

A. Karakurkchi
PhD, Head of Research Laboratory*
E-mail: anyutikukr@gmail.com
M. Sakhnenko
Doctor of Technical Sciences, Professor,
Head of Department
Department of Physical Chemistry**
E-mail: sakhnenko@kpi.kharkov.ua
M. Ved
Doctor of Technical Sciences, Professor
Department of General and Inorganic Chemistry**
E-mail: vmv@kpi.kharkov.ua
A. Horokhivskyi
Researcher*
E-mail: gorohivskiy86@gmail.com
A. Galak
PhD
Department of Physical Chemistry**
E-mail: galak79@gmail.com
*Research Laboratory of Military Training Faculty**
**National Technical University
«Kharkiv Polytechnic Institute»
Kyrpychova str., 2, Kharkiv, Ukraine, 61002

Досліджено формування кобальтовмісних оксидних покривів методом плазмово-електролітичного оксидування силуміну АК12М2МгН у пірофосфатних електролітах. Показано, що варіювання концентрації кобальту сульфату в розчині впливає на робочі параметри ПЕО. Встановлено, що склад та морфологія сформованих оксидних шарів залежать від співвідношення компонентів електроліту. Це дозволяє керувати процесом інкорпорації допанта в матрицю оксиду алюмінія. Обгрунтовано склад пірофосфатного електроліту для одержання оксидних покривів, збагачених каталітичним компонентом

Ключові слова: оксидний покрив, силумін, АК12М2МгН, плазмово-електролітичне оксидування, пірофосфатний електроліт, морфологія поверхні

Исследовано формирование кобальтосодержащих оксидных покрытий методом плазменно-электролитического оксидирования силумина АК12М2МгН в пирофосфатных электролитах. Показано, что варьирование концентрации кобальта сульфата в растворе влияет на рабочие параметры ПЭО. Установлено, что состав и морфология сформированных оксидных слоев зависят от соотношения компонентов электролита. Это позволяет управлять процессом инкорпорации допанта в матрицу оксида алюминия. Обоснован состав пирофосфатного электролита для получения оксидных покрытий, обогащенных каталитическим компонентом

Ключевые слова: оксидное покрытие, силумин, АК12М2МгН, плазменно-электролитическое оксидирование, пирофосфатный электролит, морфология поверхности

1. Introduction

The alloys of aluminum with silicon are demanded structural materials. Due to their unique physical-mechanical properties and high treatment manufacturability, they are widely used in various industries: automotive and motor engineering, heating and water supply systems, consumer goods.

High silicon content provides silumins with enhanced casting properties, higher corrosion resistance, strength and durability. At the same time, coarse-needle eutectics and primary deposition of silicon in the structure of silumins cause

embrittlement of the material. This undesirable phenomenon strengthens with an increase in the content of Si in alloy composition [1]. That is why, in order to ensure a high level of mechanical properties, it is required to use additional methods for the surface modification of such materials.

One of the approaches is to create on the material's surface ceramic-like oxide coatings by the method of plasma-electrolytic oxidizing (PEO). The technique involves the oxidizing of surface in aqueous electrolytes at high voltage under the action of short-lived electrical discharges. Under such high-energy modes, due to the implementation of electrochemical and thermochemical reactions, there occurs the formation of a highly developed oxide matrix of the base metal, which incorporates the electrolyte components [2, 3]. The advantages of a given technique of surface modification include simplicity of the equipment used, non-toxic working solutions, absence of the stage for preliminary preparation of a part, the possibility of efficient treatment of complex-shaped products. The indicated factors characterize PEO process as economical, eco-friendly and resource-saving [2].

Change in the conditions of oxidizing and in the composition of working solutions makes it possible to form oxide system with preset composition and properties.

At the same time, PEO of silumins is a rather complex process because these materials contain large amounts of alloying components and inter-metallic compounds that oxides differ in chemical properties and electric conductivity [4]. That is why studying the processes of targeted modification of surface though the formation of oxide PEO-coatings is an important practical task. Solving it would enable improvement in the operational properties of silumins and would broaden the scope of their application.

2. Literature review and problem statement

Electrochemical technologies are widely employed for the modification of surfaces of metals and alloys by forming coatings with different composition and purpose [5, 6].

PEO of valve metals is traditionally carried out in homogeneous electrolytes, which are characterized by high stability and ease of adjustment during operation and make it possible to change qualitative and quantitative composition in a wide range [2]. Using the electrolytes of a given type allows efficient treatment of alloys with different chemical composition and creation of oxide coatings doped with one or more components [3, 7]. Electrolytes-suspensions that consist of the base homogeneous electrolyte and additives from powders of different nature and dispersion degree have also been utilized [8, 9]. In this case, in addition to electrochemical and thermo-chemical transformations, the growth of coating occurs due to mechanical capture of particles from a working solution. It should be noted that the type of the electrolyte used and the nature of doping components predetermine the composition and properties of the formed oxide layer [10].

PEO of titanium in phosphoric acid with the addition of copper nitrate makes it possible to form porous coatings of titanium oxide with copper inclusions. The obtained materials possess antibacterial properties [11]. Composite coatings with photo-catalytic properties were received on titanium alloys by the oxidizing in pyrophosphate electrolytes with zirconium oxide additives [12]. To form oxide coatings with enhanced chemical and thermal resistance, surface layers of titanium and aluminum were doped with nickel and iron from the solutions of polyphosphates [13]. Plasma-electrolytic treatment of aluminum in borate electrolytes allows obtaining oxide coatings with high micro-hardness [14]. The introduction of transition metals to the composition of surface oxide layers considerably improves catalytic properties of PEO-coatings in the reactions of decomposition of toxic components [15, 16].

At the same time, still unresolved are the issues of control over composition and morphology of the formed coatings on alloys with a high content of impurities (alloying components). Surface heterogeneity of such materials and, as a consequence, different conductivity of alloy components' oxides requires correction of the used electrolyte composition, and of technological process of oxidizing.

Electrolytes with different composition are used for obtaining oxide coatings on silumins.

Paper [17] reported study of patterns of the PEO-coatings formation on aluminum alloy AA 6061 (a content of Si to 1 % by weight) when treating them in the electrolyte based on Na_2SiO_3 and KOH. It is noted that the growth of coating, as well as the ignition mechanisms of charges, change during PEO at different stages of the process. The surface morphology of obtained coatings is characterized by presence of craters, enriched with aluminum, and knotted silicon structures. A clear correlation was established between the microstructure of coatings obtained and samples' treatment time. The coatings obtained under a spark mode had many micropores scattered on the surface. The size of pores in the coating increases during transition to a micro-spark mode, their spatial intensity decreases in proportion to treatment time.

PEO of the aluminum alloy Al-7 % Si in the alkaline silicate electrolyte [18] also differs at various stages of treatment. A slowed growth of the oxide film in a pre-spark region results from the presence of silicon in the composition of treated material. Stabilization of the oxidizing technological parameters is observed in the region of micro-spark charges with a higher average growth rate of the coating achieved. The specified conditions made it possible to obtain films with a thickness exceeding 140 μm. The generated oxide layers consist of mullite, α- and γ-Al_2O_3, and amorphous phases; they demonstrate corrosion protective properties at considerable thickness of the coating.

Authors of [19] performed PEO of alloy Al-Si samples with a silicon content of 27–32 % by weight in the alkaline silicate electrolyte. It was established that in the course of treatment, the glow of discharges occurs in a spark and a micro-arc region mainly at the boundaries of silicon inclusions. This, as a consequence, inhibits the growth of a coating on the sample's surface, and formed oxide layer is non-homogeneous. Surface morphology is characterized by the presence of large dendrites of silicon oxide. In order to obtain uniform layers, treatment period must last for 60 minutes and longer.

Similar patterns were established also in the study of PEO process of the cast piston Al-Si alloy with a silicon content of 12 % by weight [20]. To optimize the plasma-electrolytic treatment, the authors used a silicate electrolyte with sodium phosphate additives. It was established that particles of silicon in the alloy composition and eutectic Si-phases inhibit the oxidizing of aluminum and exert considerable influence on the morphology and composition of obtained coatings.

It is noted that the silicate content in the electrolyte composition affects the duration of PEO-treatment process of high-silicon aluminum alloys, composition and thickness of the oxide coatings obtained [21]. This allows control over

the technological process of silumin PEO at various concentrations of the electrolyte components.

Oxide coatings can be obtained using the method of PEO on silumins under galvanostatic mode and at polarization by pulse current. In this case, the mode of d.c. current leads to the «healing» of defects in oxide coatings and the formation of surface with a more uniform morphology [22].

PEO-coatings, formed in the silicate electrolytes, possess enhanced micro- hardness and corrosion resistance as compared with untreated surface [18, 22]. However, due to the large content of silicon in the surface layers, these parameters are not optimal.

In order to expand the range of functional properties of PEO-coatings on silumins, it is expedient to apply complex electrolytes.

In [23], author used, in order to obtain oxide coatings on the aluminum alloy 1050, silicate-alkaline electrolytes with additives of sodium tetraborate, trilon B, acetic acid and acetates of transition metals. The coatings were formed by alternating current at an average density of 100 mA/cm^2. Under given conditions, the author obtained uniform oxide layers with a content of dopants at 1.1–5.43 at. %. At the same time, the coatings contain 8.46–13.5 at. % of silicon and 8.06–32.62 at. % of carbon, which is explained by the thermolysis of electrolyte components during PEO.

In paper [24], oxide coatings doped with magnesium, manganese and zinc on the alloy AD1 were formed from polyphosphate electrolytes. It was established that the content of doping elements in a coating is proportional to the ratio of concentrations of polyphosphate and a metal salt. Phase composition of obtained oxide layers changes depending on the duration of PEO and component composition of the working solution.

Polyphosphate electrolytes were also used for obtaining oxide coatings on the aluminum alloy AMtsM with a high content of dopants [25]. It is shown that the formation of polyphosphate complexes with metals-dopants contributes to their proportional inclusion to the formed oxide films.

Thus, from the point of view of the effectiveness of surface modification of silumins, it is advisable for their treatment to use electrolytes based on complex compounds, specifically polyphosphates. This makes it possible, in the process of oxidizing, to remove a large part of alloying components from the surface layer and create conditions for the incorporation of dopants to the composition of the formed oxide coating.

3. The aim and objectives of the study

The aim of present work is to study the influence of the components concentration in pyrophosphate electrolyte on the composition and morphology of cobalt-containing oxide coatings on AK12M2MgN. This would optimize the process of obtaining materials with a different content of the catalytically-active component.

To achieve the aim, the following tasks have been set:

– to explore a change in the parameters of plasma-electrolytic oxidizing of AK12M2MgN in electrolytes with a varied content of components;

– to study dependence of the composition and morphology of formed oxide coatings surface on the concentration of electrolyte components;

– to substantiate the composition of pyrophosphate electrolyte in order to form oxide PEO-coatings with a preset content of cobalt and surface morphology.

4. Technique for obtaining oxide coatings on AK12M2MgN, for studying their composition and morphology

4. 1. Method for obtaining

Cobalt-containing oxide coatings were formed on samples of the aluminum cast alloy AK12M2MgN with a working area of 0.2 dm^2. Chemical composition of the alloy is given in Table 1.

Table 1

Chemical composition of the alloy AK12M2MgN (GOST1583), % by weight

Al	Si	Mn	Mg	Ni	Fe
79.5–85.55	11–13	0.3–0.6	0.8–1.3	0.8–1.3	to 0.8
Cr	Ti	Cu	Pb	Zn	Sn
to 0.2	0.05–0.2	1.5–3.0	to 0.1	to 0.5	to 0.02
Impurities					
total 1.3					

Plasma-electrolytic oxidizing was carried out in alkaline electrolytes of different composition (Table 2).

Table 2

Electrolytes for PEO of the alloy AK12M2MgN

Electrolyte number	Composition, mol/dm^3	
	$K_4P_2O_7$	$CoSO_4$
1	0.4	0.05
2	0.4	0.1
3	0.6	0.2

Working solutions for the research were prepared using certified reagents of grade «chemically pure» and distilled water. Electrochemical treatment was conducted under galvanostatic mode. We used a laboratory installation for the formation of coatings. It consisted of the industrial stabilized d.c. current source B5-50, electrolytic cell, instruments to monitor working parameters of the process (ammeter and voltmeter). We used forced cooling and electrolyte agitation in the cell.

The treatment current density was fixed at the level of 5 A/dm^2, voltage – to 160 C. Stages of PEO were controlled visually and recorded according to the instruments readouts. The coatings were formed during 25 minutes. Temperature of the electrolyte was maintained within 20–25 °C.

Preliminary preparation of the surface of samples involved mechanical machining (polishing), degreasing, rinsing with water and drying at a temperature of 30 °C.

4. 2. Methods of the study of oxide coatings

Surface morphology of the obtained oxide coatings was investigated using the scanning electron microscope ZEISS EVO 40XVP (Germany). Topography of the coating surface was studied by the method of atomic-force microscopy using the microscope NT-206, the probe CSC-37. Chemical composition of the surface oxide layers was determined using the energy-dispersion spectrometer Oxford INCA Energy 350 (United Kingdom) with the integrated programming environment SmartSEM.

5. Results of the formation of oxide coatings on AK12M2MgN

Chronograms of the forming voltage of cobalt-containing oxide coatings on AK12M2MgN in electrolytes with a varied salt of cobalt take the classical form, divided into characteristic regions: pre-spark, spark, micro-arc, and arc discharges (Fig. 1).

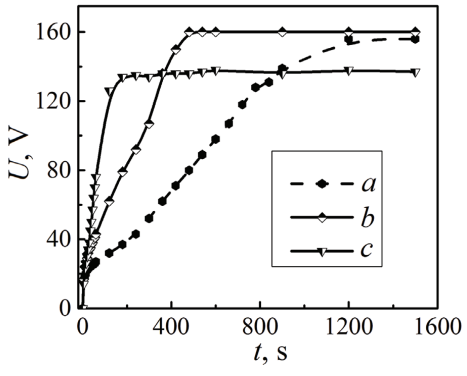

Fig. 1. Chronograms of forming voltage during PEO of AK12M2MgN in electrolytes of the following composition, mol/dm^3: a – 0.4 $K_4P_2O_7$, 0.05 $CoSO_4$; b – 0.4 $K_4P_2O_7$, 0.1 $CoSO_4$; c – 0.6 $K_4P_2O_7$, 0.2 $CoSO_4$

U-t dependence sections in a pre-spark area are almost linear, which is explained by an increase in the aluminum oxide film thickness and its enhanced resistance. Time to the sparking regime for the examined electrolytes increases from 2 to 11 minutes in proportion to a decrease in $CoSO_4$ content in the solution from 0.2 to 0.05 mol/dm^3. The sparking voltage in this case is 115–120 V, and the resulting forming voltage is 140–160 V.

The dependence of rate of voltage change dU/dt on forming voltage U reflects the formation kinetics and allows us to more accurately determine the voltage of sparking start 45–50 V (Fig. 2). In addition, it becomes apparent that in the solutions containing 0.4 mol/dm^3 of potassium pyrophosphate the fluctuations on dU/dt–U dependences are significantly lower (Fig. 2, *a, b*) compared to the more concentrated solution (Fig. 2, *c*).

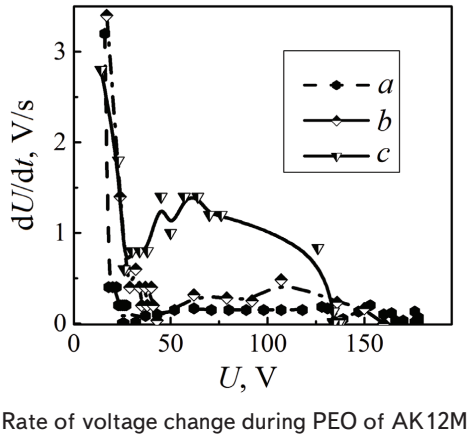

Fig. 2. Rate of voltage change during PEO of AK12M2MgN in electrolytes with different composition, mol/dm^3: a – 0.4 $K_4P_2O_7$, 0.05 $CoSO_4$; b – 0.4 $K_4P_2O_7$, 0.1 $CoSO_4$; c – 0.6 $K_4P_2O_7$, 0.2 $CoSO_4$

An analysis of the oxide coatings composition, averaged by the surface, indicates that the aluminum oxide matrix includes cobalt oxides and remelted electrolyte components (Fig. 3).

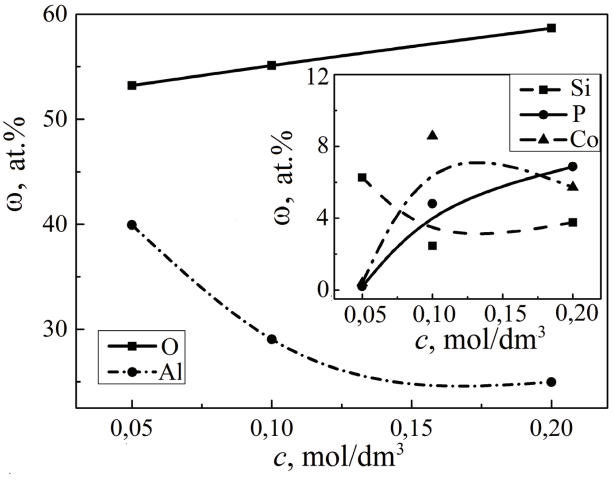

Fig. 3. Dependence of gross composition of PEO-coatings on AK12M2MgN on the concentration of cobalt sulfate in a working electrolyte

It was established that an increase in the $CoSO_4$ concentration in the electrolyte contributes to the enrichment of surface layers with cobalt with a simultaneous decrease in the content of silicon in them. Coatings with the highest cobalt content were obtained from solution with a $CoSO_4$ concentration at 0.1 mol/dm^3. The content of silicon in this case is minimal and is only 2.1 at. %.

The variation of cobalt content in the solutions and, accordingly, in the coatings as well, obtained by the plasma-electrolytic treatment of AK12M2MgN, causes a change in the surface morphology, from uniformly rough (Fig. 4, *a*) to uniform large-globular (Fig. 4, *b*) to non-uniform globular-mosaic (Fig. 4, *c*).

SEM images of the examined coatings visualize plots with varying topography. Plot 1 is defined as a protrusion of the mixed oxide coating, or a globule. Plot 2 is positioned as a plateau and corresponds to the matrix of oxides of the treated material. These are the plots (Fig. 4, *a–c*) that are selected for a comparative analysis of composition of the obtained coatings.

The results obtained (Fig. 5) indicate that the cobalt content on the protrusions of coatings is higher than that on the plateau, and ranges from 1.2 to 23.3 at. % depending on the composition of an electrolyte. Inverse dependence is observed in aluminum and silicon distribution on the surface. Thus, on the surface of globules silicon content is 1.8–3.9, aluminum – 15.9–33.4 at. %; silicon concentration on the plateau is 2.6–6.3, aluminum – 26.7–40.0 at. %. The content of oxygen on all plots reflects the formation of nonstoichiometric cobalt oxides.

Plasma-electrolytic treatment of the alloy AK12M2MgN in pyrophosphate electrolytes with cobalt sulfate additives results in the formation of a three-dimensional structure [26]. High level of surface development of the obtained coatings is confirmed by the results of study into topography of surface layers using the contact method (Fig. 6).

The obtained results allow us to determine the ways to control the composition and surface morphology of the formed oxide layers during treatment of AK12M2MgN in pyrophosphate electrolytes.

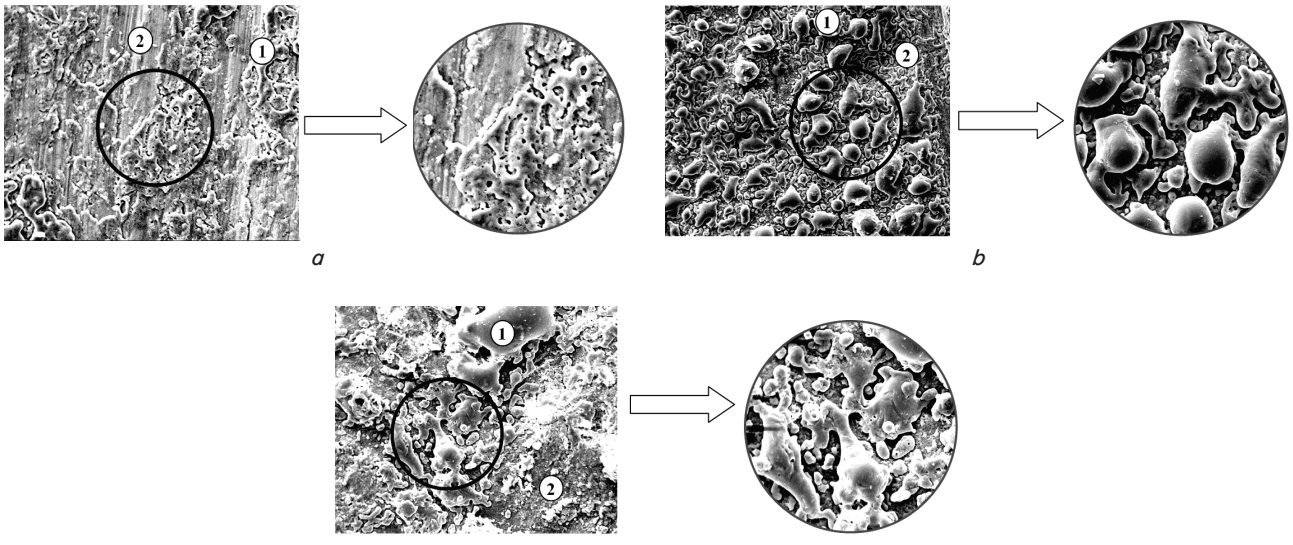

Fig. 4. Surface morphology of oxide coatings on AK12M2MgN, formed on electrolytes of following composition, mol/dm^3: *a* – 0.4 $K_4P_2O_7$, 0.05 $CoSO_4$; *b* – 0.4 $K_4P_2O_7$, 0.1 $CoSO_4$; *c* – 0.6 $K_4P_2O_7$, 0.2 $CoSO_4$. Magnification ×500 and 1000

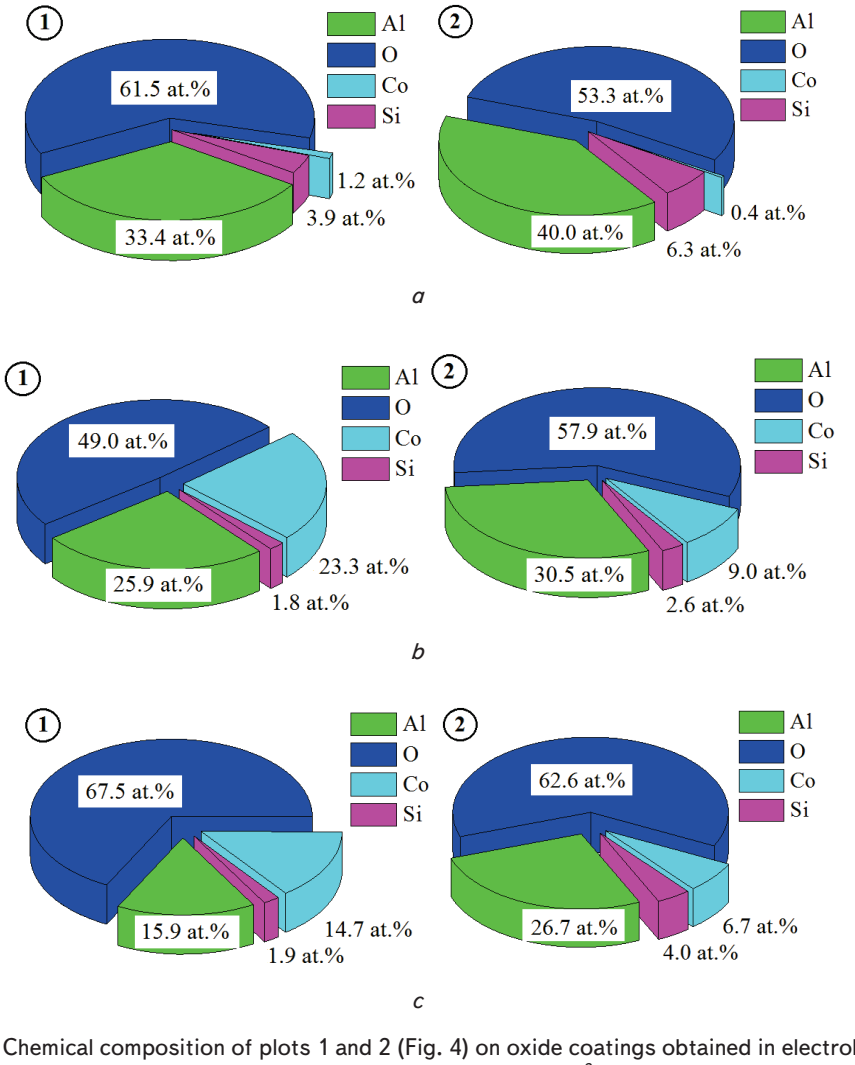

Fig. 5. Chemical composition of plots 1 and 2 (Fig. 4) on oxide coatings obtained in electrolytes of following composition, mol/dm^3: *a* – 0.4 $K_4P_2O_7$, 0.05 $CoSO_4$; *b* – 0.4 $K_4P_2O_7$, 0.1 $CoSO_4$; *c* – 0.6 $K_4P_2O_7$, 0.2 $CoSO_4$

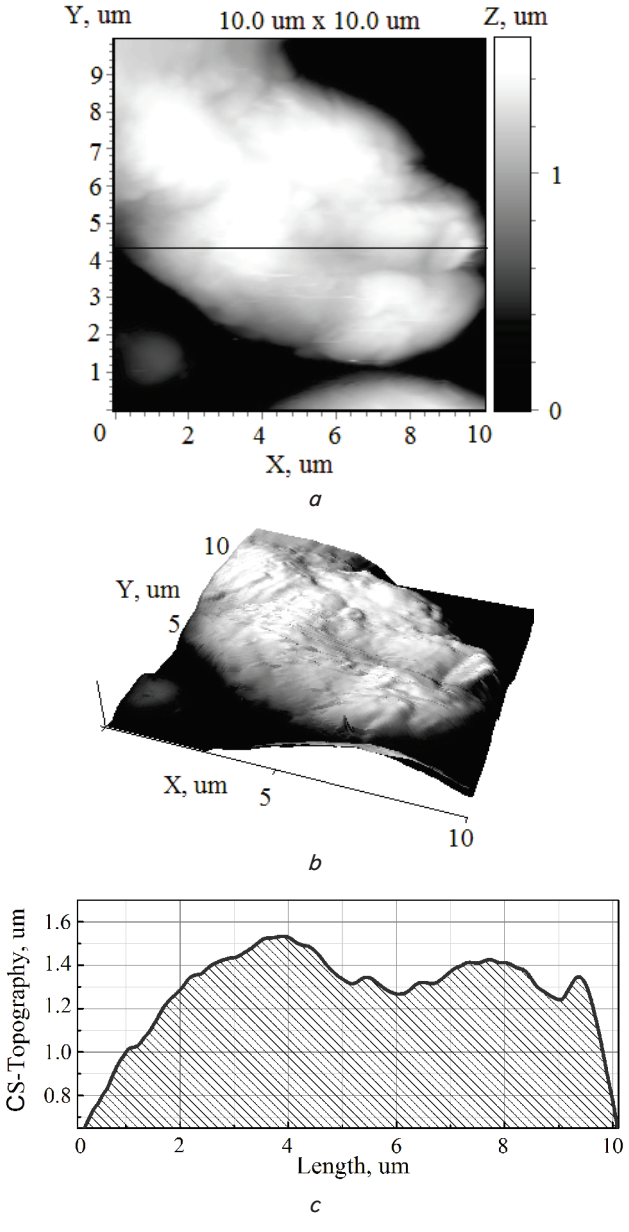

Fig. 6. Surface of the cobalt-containing oxide PEO-coating on AK12M2MgN obtained from electrolyte 0.4 mol/dm^3 $K_4P_2O_7$, 0.1 mol/dm^3 $CoSO_4$: *a* – 2D-map, *b* – 3D-map, *c* – cross-section profile. Scanning area 10×10 μm

6. Discussion of the effect of electrolyte components ratio on the structure and morphology of cobalt-containing oxide coatings

The formation of an oxide layer on the alloy AK12M2MgN in pyrophosphate electrolytes, in accordance with contemporary views on the mechanism of PEO, occurs at sequential implementation of the following stages [27]:

– formation of the dielectric phase oxide Al_2O_3 in line with the electrochemical mechanism (a pre-spark mode);

– breakdown of Al_2O_3 film (start of sparking);

– gaseous-phase and thermo-chemical reactions involving the oxide of base metal and electrolyte components (a micro-arc mode);

– polymorphic transformations of oxide phases (an arc mode).

The alloy AK12M2MgN is characterized by high content of alloying components (including silicon) and the heterogeneity of their distribution on the surface. That is why the process of plasma-electrolytic oxidizing depends to a large extent on the composition of the electrolyte.

At the early stages of oxidizing, there occurs, in the alkaline pyrophosphate electrolyte, the anodic dissolution of alloying components from the surface with the formation of oxoanions (SiO_3^{2-}) or sufficiently strong complexes $[MP_2O_7]^{x-}$ (M is the alloying metal). The result is the homogenization of surface of the treated alloy when the preconditions are created for the incorporation of cobalt to the composition of the formed oxide layer [28].

During treatment of samples in electrolyte 1 (Table 3) whose ratio between concentrations of ligand and cobalt is 8:1, entering a sparking mode occurs only on minute 11. A sloping forming dependence (Fig. 1, *a*) and low rate of voltage change at U>115 V (Fig. 2, *a*) indicate the competition between processes of aluminum oxide formation/dissolution and weak intensity of thermo-chemical reactions. That is why the incorporation of cobalt to the composition of the formed oxide layer is insignificant, its content does not exceed 2 at. %, and a large amount of silicon remains in the composition of a surface layer (Fig. 3, *a*).

With an increase in the $CoSO_4$ content in a working solution to 0.1 mol/dm^3 (electrolyte 2, concentration ratio $K_4P_2O_7$:$CoSO_4$ is 4:1), duration of entering a sparking mode is reduced by 2 times while maintaining high working formation voltage (Fig. 1, *b*). The presence of fluctuations on $\mathbf{d}U/\mathbf{d}t$–U dependences (Fig. 2, *b*) indicates the formation on the surface oxides with different specific resistance and thermal stability, as well as the intensification of thermo-chemical reactions [29]. This makes it possible to obtain coatings with a high content of dopants and lower amount of silicon (Fig. 3).

The process of sample oxidizing in electrolyte 3 (ratio of concentrations between ligand and cations of cobalt is 3:1) is characterized by the rapid formation of a barrier aluminum oxide. Entering a sparking mode occurs on minute 2 of the treatment (Fig. 1, *c*), however, the voltage of a micro-arc mode does not exceed 140 V. Dependence dU/dt–U differs from the previous ones by the existence of significant fluctuations and sharp decline in dU/dt when voltage reaches a micro-arc mode (Fig. 2, *c*). Obviously, at a high concentration of pyrophosphate, there is a competition between the reactions of formation/dissolution of mixed oxides, as well as the accumulation of insoluble salts in a near-electrode layer, which reduces process stability [30]. Cobalt is included in the generated oxide coating in the amount of 15 at. %, but the content of silicon in the surface layer remains significant (Fig. 3, *c*).

A comparative analysis of the forming dependences and the rate of voltage change reveal that the formation rate of a cobalt-containing oxide film grows, but a sparking start time decreases, with an increase in the $CoSO_4$ concentration in a working solution.

Given these factors, optimal parameters for obtaining coatings with high dopants content and a low concentration of impurities imply entering a sparking mode swiftly and higher voltage in a micro-arc regime. The assumption we made is confirmed by data on the chemical composition of oxide coatings obtained from electrolytes with a different components ratio (Fig. 3). The dynamics of basic compo-

nents content in surface layer adequately agrees with the proposed mechanism for the coatings formation in the alkaline solutions of pyrophosphates [31].

The incorporation of dopants to the generated oxide coating affects the surface layer morphology (Fig. 4). As a result of plasma-electrolytic treatment of AK12M2MgN samples in the alkaline cobalt-pyrophosphate solutions we obtained oxide layers with high adhesion to the base metal. The incorporation of cobalt to the coating composition leads to the formation of blue-purple color spheroids (globules) on the surface. At a sufficiently big quantity, they merge and form mosaic structures, which cover almost the entire surface of a sample [32].

The surface morphology of the samples treated in electrolyte 1 (Fig. 4, *a*) matches the structure of a barrier aluminum oxide with the initial stage of the island incorporation of cobalt. This is confirmed by the results of chemical composition analysis on the plots with different topography (Fig. 5, *a*).

Oxidizing in electrolyte 2 ensures the formation of a highly developed surface with a mosaic structure (Fig. 4, *b*). Sphere-like globules are almost evenly distributed across the sample surface with the concentration of cobalt not exceeding 20 at. % (Fig. 5, *b*). At the same time, the content of catalytically-active component on plateau is 2.5 times lower and is only 9 at. %. During plasma-electrolytic treatment in electrolyte 3, oxide coatings are formed with large cobalt-containing spheroids (Fig. 4, *c*). In this case, their quantity on the examined surface is not too large. This is reflected by the lower content of catalytically-active component on the protrusions of the coating and on the plateau (Fig. 5, *c*). The results obtained are in full agreement with the kinetic patterns and make it possible to determine a rational composition of the electrolyte in order to obtain oxide coatings with preset composition and morphology [31].

Results of atomic-force microscopy confirm that surface of the system $Al{\cdot}Al_2O_3{\cdot}CoO_x$ is a micro-globular one (Fig. 6, *a*). Mixed oxide coatings consist of a multitude of spheroid conglomerates whose average size is 1–2 μm, which merge and form plots of smooth surface with spherical agglomerates of 6–8 μm (Fig. 6, *b*). Roughness and true surface of the obtained oxide coating is visualized from the cross-section of agglomerate (Fig. 6, *c*) and is optimal for the realization of catalytic processes [33].

Based on the research performed for the purpose of obtaining mixed oxide layers, on AK12M2MgN, under PEO mode, with a high content of cobalt and a developed surface, we recommended using the electrolyte of the following composition, mol/dm^3: $0.4{\cdot}K_4P_2O_7$, $0.1{\cdot}CoSO_4$.

The obtained cobalt-containing oxide coatings could be applied in toxins neutralization technologies, specifically, in air and water purification systems, to reduce the toxicity of gas emissions from internal combustion engines [26, 34].

7. Conclusions

1. We studied a change in the parameters of plasma-electrolytic oxidizing of the alloy AK12M2MgN in pyrophosphate electrolytes with a varied content of cobalt sulfate. It was established that the concentration ratio of cobalt salt and ligand affect the time required to enter a sparking mode and working formation voltage.

2. It was established that a change in the cobalt cations concentration in the electrolyte makes it possible to control the process of incorporation of cobalt oxide to the matrix of aluminum oxide. It is shown that an increase in the $CoSO_4$ concentration in the electrolyte contributes the enrichment of surface oxide layers with cobalt. The inclusion of cobalt to oxide layers composition leads to the formation of a mosaic three-dimensional surface structure.

3. The formation of PEO-coatings on AK12M2MgN with a maximum content of cobalt at minimizing the impurities and with a developed surface is expedient to carry out from the electrolyte with a composition of 0.4 mol/dm^3 $K_4P_2O_7$, 0.1 mol/dm^3 $CoSO_4$.

References

1. Zolotorevsky, V. S. Casting Aluminum Alloys [Text] / V. S. Zolotorevsky, N. A. Belov, M. V. Glazoff. – Elsevier Science, 2007. – 544 p. doi: 10.1016/b978-0-08-045370-5.x5001-9
2. Suminov, I. V. Plazmenno-elektroliticheskoe modifitsirovanie poverhnosti metallov i splavov. Vol. 2 [Text] / I. V. Suminov, P. N. Belkin, A. V. Eperfel'd, V. B. Lyudin, B. L. Krit, A. M. Borisov; I. V. Suminov (Ed.). – Moscow: Tekhnosfera, 2011. – 512 p.
3. Gupta, P. Electrolytic plasma technology: Science and engineering – An overview [Text] / P. Gupta, G. Tenhundfeld, E. O. Daigle, D. Ryabkov // Surface and Coatings Technology. – 2007. – Vol. 201, Issue 21. – P. 8746–8760. doi: 10.1016/j.surfcoat.2006.11.023
4. Krishtal, M. M. Oxide Layer Formation by Micro-Arc Oxidation on Structurally Modified Al-Si Alloys and Applications for Large-Sized Articles Manufacturing [Text] / M. M. Krishtal // Advanced Materials Research. – 2009. – Vol. 59. – P. 204–208. doi: 10.4028/www.scientific.net/amr.59.204
5. Rudnev, V. S. Aluminum- and titanium-supported plasma electrolytic multicomponent coatings with magnetic, catalytic, biocide or biocompatible properties [Text] / V. S. Rudnev, I. V. Lukiyanchuk, M. S. Vasilyeva, M. A. Medkov, M. V. Adigamova, V. I. Sergienko// Surface and Coatings Technology. – 2016. – Vol. 307. – P. 1219–1235. doi: 10.1016/j.surfcoat.2016.07.060
6. Ved, M. Catalytic properties of binary and ternary alloys based on silver [Text] / M. Ved, M. Glushkova, N. Sakhnenko // Functional Materials. – 2013. – Vol. 20, Issue 1. – P. 87–91. doi: 10.15407/fm20.01.087
7. Rogov, A. B. Peculiarities of iron-containing microplasma coating deposition on aluminum in homogeneous electrolyte [Text] / A. B. Rogov, A. I. Slonova, V. R. Shayapov // Applied Surface Science. – 2012. – Vol. 261. – P. 647–652. doi: 10.1016/j.apsusc.2012.08.075
8. Malyshev, V. N. Features of Microarc Oxidation Coatings Formation Technology in Slurry Electrolytes [Text] / V. N. Malyshev, K. M. Zorin // Applied Surface Science. – 2007. – Vol. 254, Issue 5. – P. 1511–1516. doi: 10.1016/j.apsusc.2007.07.079
9. Borisov, A. M. Microarc oxidation in slurry electrolytes: A review [Text] / A. M. Borisov, B. L. Krit, V. B. Lyudin, N. V. Morozova, I. V. Suminov, A. V. Apelfeld // Surface Engineering and Applied Electrochemistry. – 2016. – Vol. 52, Issue 1. – P. 50–78. doi: 10.3103/s106837551601004x

10. Sakhnenko, N. A study of synthesis and properties of manganese-containing oxide coatings on alloy VT1-0 [Text] / N. Sakhnenko, M. Ved, A. Karakurkchi, A. Galak // Eastern-European Journal of Enterprise Technologies. – 2016. – Vol. 3, Issue 5 (81). – P. 37–43. doi: 10.15587/1729-4061.2016.69390
11. Rokosz, K. GDOES, XPS, and SEM with EDS analysis of porous coatings obtained on titanium after plasma electrolytic oxidation [Text] / K. Rokosz, T. Hryniewicz, S. Raaen, P. Chapon, L. Dudek // Surface and Interface Analysis. – 2016. – Vol. 49, Issue 4. – P. 303–315. doi: 10.1002/sia.6136
12. Sakhnenko, N. D. Characterization and photocatalytic activity of Ti/TinOm·ZrxOy coatings for azo-dye degradation [Text] / N. D. Sakhnenko, M. V. Ved, V. V. Bykanova // Functional materials. – 2014. – Vol. 21, Issue 4. – P. 492–497. doi: 10.15407/fm21.04.492
13. Rudnev, V. S. Iron- and nickel-containing oxide-phosphate layers on aluminum and titanium [Text] / V. S. Rudnev, V. P. Morozova, T. A. Kaidalova, P. M. Nedozorov // Russian Journal of Inorganic Chemistry. – 2007. – Vol. 52, Issue 9. – P. 1350–1354. doi: 10.1134/s0036023607090069
14. Li, H. X. Characterization of Al2O3 ceramic coatings on 6063 aluminum alloy prepared in borate electrolytes by micro-arc oxidation [Text] / H. X. Li, V. S. Rudnev, X. H. Zheng, T. P. Yarovaya, R. G. Song // Journal of Alloys and Compounds. – 2008. – Vol. 462, Issue 1-2. – P. 99–102. doi: 10.1016/j.jallcom.2007.08.046
15. Sakhnenko, M. Examining the formation and properties of TiO2 oxide coatings with metals of iron triad [Text] / M. Sakhnenko, A. Karakurkchi, A. Galak, S. Menshov, O. Matykin // Eastern European Journal of Enterprise Technologies. – 2017. – Vol. 2, Issue 11 (86). – P. 4–10. doi: 10.15587/1729-4061.2017.97550
16. Lukiyanchuk, I. V. Plasma electrolytic oxide layers as promising systems for catalysis [Text] / I. V. Lukiyanchuk, V. S. Rudnev, L. M. Tyrina // Surface and Coatings Technology. – 2016. – Vol. 307. – P. 1183–1193. doi: 10.1016/j.surfcoat.2016.06.076
17. Dehnavi, V. Production of ceramic coatings on AA6061 aluminium alloy using plasma electrolytic oxidation [Text] / V. Dehnavi, B. L. Luan, X. Y. Liu, D. W. Shoesmith, S. Rohani // Materials Science and Technology (MS&T 2013) Conference. – Montreal, 2013. – P. 2247–2254.
18. Xue, W. Preparation of anti-corrosion films by microarc oxidation on an Al–Si alloy [Text] / W. Xue, X. Shi, M. Hua, Y. Li // Applied Surface Science. – 2007. – Vol. 253, Issue 14. – P. 6118–6124. doi: 10.1016/j.apsusc.2007.01.018
19. Xu, F. The mechanism of PEO process on Al–Si alloys with the bulk primary silicon [Text] / F. Xu, Y. Xia, G. Li // Applied Surface Science. – 2009. – Vol. 255, Issue 23. – P. 9531–9538. doi: 10.1016/j.apsusc.2009.07.090
20. Wang P. Ceramic coating formation on high Si containing Al alloy by PEO process [Text] / P. Wang, J. P. Li, Y. C. Guo, Z. Yang, J. L. Wang // Surface Engineering. – 2016. – Vol. 32, Issue 6. – P. 428–434. doi: 10.1179/1743294415y.0000000003
21. Dudareva, N. Yu. The Structure of Plasma-Electrolytic Coating Formed on Al–Si alloys by the Micro-Arc Oxidation Method [Text] / N. Yu. Dudareva, M. M. Abramova // Protection of Metals and Physical Chemistry of Surfaces. – 2016. – Vol. 52, Issue 1. – P. 128–132. doi: 10.1134/s2070205116010093
22. Dai, L. Anti-corrosion and wear properties of plasma electrolytic oxidation coating formed on high Si content Al alloy by sectionalized oxidation mode [Text] / L. Dai, W. Li, G. Zhang, N. Fu, Q. Duan // IOP Conference Series: Materials Science and Engineering. – 2017. – Vol. 167. – P. 012063. doi: 10.1088/1757-899x/167/1/012063
23. Rogov, A. B. Plasma electrolytic oxidation of A1050 aluminium alloy in homogeneous silicate-alkaline electrolytes with edta 4 – complexes of Fe, Co, Ni, Cu, La and Ba under alternating polarization conditions [Text] / A. B. Rogov // Materials Chemistry and Physics. – 2015. – Vol. 167. – P. 136–144. doi: 10.1016/j.matchemphys.2015.10.020
24. Boguta, D. L. On Composition of Anodic-Spark Coatings Formed on Aluminum Alloys in Electrolytes with Polyphosphate Complexes of Metals [Text] / D. L. Boguta, V. S. Rudnev, T. P. Yarovaya, T. A. Kaidalova, P. S. Gordienko // Russian Journal of Applied Chemistry. – 2002. – Vol. 75, Issue 10. – P. 1605–1608. doi: 10.1023/a:1022263331315
25. Rudnev, V. S. Multiphase Anodic Layers and Prospects of Their Application [Text] / V. S. Rudnev // Protection of Metals. – 2008. – Vol. 44, Issue 3. – P. 263–272. doi: 10.1134/s0033173208030089
26. Ved', M. V. Functional mixed cobalt and aluminum oxide coatings for environmental safety [Text] / M. V. Ved', N. D. Sakhnenko, A. V. Karakurkchi, T. Yu. Myrna // Functional Materials. – 2017. – Vol. 24, Issue 2. – P. 303–310. doi: 10.15407/fm24.02.303
27. Rakoch, A. G. Model concepts on the mechanism of microarc oxidation of metal materials and the control over this process [Text] / A. G. Rakoch, V. V. Khokhlov, V. A. Bautin, N. A. Lebedeva, Yu. V. Magurova, I. V. Bardin // Protection of Metals. – 2006. – Vol. 42, Issue 2. – P. 158–169. doi: 10.1134/s003317320602010x
28. Ved', M. V. Modeling of the surface treatment of passive metals [Text] / M. V. Ved', M. D. Sakhnenko, O. V. Bohoyavlens'ka, T. O. Nenastina // Materials Science. – 2008. – Vol. 44, Issue 1. – P. 79–86. doi: 10.1007/s11003-008-9046-6
29. Sakhnenko, N. D. Formation of coatings of mixed aluminum and manganese oxides on the AL25 alloy [Text] / N. D. Sakhnenko, M. V. Ved', D. S. Androshchuk, S. A. Korniy // Surface Engineering and Applied Electrochemistry. – 2016. – Vol. 52, Issue 2. – P. 145–151. doi: 10.3103/s1068375516020113
30. Cho, J.-Y. Influence of potassium pyrophosphate in electrolyte on coated layer of AZ91 Mg alloy formed by plasma electrolytic oxidation [Text] / J.-Y. Cho, D.-Y. Hwang, D.-H. Lee, B. Yoo, D.-H. Shin // Transactions of Nonferrous Metals Society of China. – 2009. – Vol. 19, Issue 4. – P. 824–828. doi: 10.1016/s1003-6326(08)60358-1
31. Sakhnenko, N. D. Nanoscale Oxide PEO Coatings Forming from Diphosphate Electrolytes [Text] / N. D. Sakhnenko, M. V. Ved, A. V. Karakurkchi // Nanophysics, Nanomaterials, Interface Studies, and Applications: Selected Proceedings of the 4th International

Conference Nanotechnology and Nanomaterials (NANO-2016). – Springer International Publishing AG, 2017. – P. 159–184. doi: 10.1007/978-3-319-56422-7_38

32. Yar-Mukhamedova, G. Sh. Mixed alumina and cobalt containing plasma electrolytic oxide coatings [Text] / G. Sh. Yar-Mukhamedova, M. V. Ved, A. V. Karakurkchi, N. D. Sakhnenko // IOP Conference Series: Materials Science and Engineering. – 2017. – Vol. 213. – P. 012020. doi: 10.1088/1757-899x/213/1/012020
33. Senesi, G. S. AFM Applications to the Analysis of Plasma-Treated Surface Growth and Nanocomposite Materials [Text] / G. S. Senesi, A. Massaro // Current Nanoscience. – 2016. – Vol. 12, Issue 2. – P. 202–206. doi: 10.2174/1573413711666150928194029
34. Karakurkchi, A. Application of oxide-metallic catalysts on valve metals for ecological catalysis [Text] / A. Karakurkchi, M. Sakhnenko, M. Ved, A. Galak, S. Petrukhin // Eastern-European Journal of Enterprise Technologies. – 2017. – Vol. 5, Issue 10 (89). – P. 12–18. doi: 10.15587/1729-4061.2017.109885

Досліджено електрохімічні властивості зносо- і корозійностійких покриттів та їх вплив на процеси тертя та зношування деталей дифузійних апаратів цукрових заводів. Встановлено вплив температури і складу технологічного середовища, електрохімічних характеристик захисних покриттів на опір деталей спрацюванню в умовах корозійно-механічного зношування. Визначено основні закономірності зношування та корозії деталей в технологічних середовищах

Ключові слова: захисні покриття, дифузійний сік, електрохімічні властивості, корозійно-механічне зношування

Исследованы электрохимические свойства износо- и коррозионностойких покрытий и их влияние на процессы трения и изнашивания деталей диффузионных аппаратов сахарных заводов. Установлено влияние температуры и состава технологической среды, электрохимических характеристик защитных покрытий на сопротивление деталей разрушению в условиях коррозионно-механического изнашивания. Определены основные закономерности изнашивания и коррозии деталей в технологических средах

Ключевые слова: защитные покрытия, диффузный сок, электрохимические свойства, коррозионно-механическое изнашивание

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ANALYSIS AND CHOICE OF COATINGS FOR INCREASING THE DURABILITY OF PARTS OF DIFFUSION UNITS OF SUGAR PLANTS

Yu. Sukhenko
Doctor of Technical Sciences,
Professor, Head of Department
Department of Processes and equipment
for processing of agricultural production**
E-mail: suhenko@ukr.net
N. Miedviedieva
PhD, Associate Professor*
E-mail: medvedeva-natali@ukr.net
V. Sukhenko
Doctor of Technical Sciences,
Professor, Head of the Department*
E-mail: vladsuhenko@gmail.com
*Department of Standardization and certifying
of agricultural products**
**National University of Life and
Environmental Sciences of Ukraine
Heroiv Oborony str., 15, Kyiv, Ukraine, 03041

1. Introduction

Aggressive technological liquids affect large quantity of metal parts of sugar plants equipment. Their influence causes intense corrosion and mechanical wear. In some cases, intensity of wear is so high that parts of equipment cannot hold out a work season of a sugar factory. This happens because of especially difficult operating conditions in aggressive media directly, in particular in diffusion juice, washing and disinfecting solutions, etc.

Friction of metals in active liquid media has specific features. Namely, deformation process and destruction of conjugate surfaces affect electrochemical factors significantly [1]. The tribocorrosion covers a science of surface transformations and combines mechanical and chemical interactions between a body, a counter body, interphase medium and medium, which includes friction, greasing, wear and tribological activated chemical and electrochemical reactions [2].

Friction in aggressive media accelerates corrosion processes significantly. Acid, alkaline and neutral technological